



TITLE:

Synthesis, Thermal Stability, Structural Features and Electromagnetic Properties of  $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+d}$  ( $0 \leq x \leq 0.4$ ) (SOLID STATE CHEMISTRY-Quantum Spin Fluids)

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CITATION:

Niinae, T. ...[et al]. Synthesis, Thermal Stability, Structural Features and Electromagnetic Properties of  $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+d}$  ( $0 \leq x \leq 0.4$ ) (SOLID STATE CHEMISTRY-Quantum Spin Fluids). ICR Annual Report 1999, 5: 18-19

ISSUE DATE:

1999-03

URL:

<http://hdl.handle.net/2433/65199>

RIGHT:

# Synthesis, Thermal Stability, Structural Features and Electromagnetic Properties of $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+\delta}$ ( $0 \leq x \leq 0.4$ )

T. Niinae and Y. Ikeda

The thermal stability and structural modulation were studied systematically in a wide range of  $0 \leq x \leq 0.4$  for the 2201 phase in the Bi-Sr-Cu-O system,  $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+\delta}$ , and it was found that these properties varied remarkably at  $x \approx 0.1$ . Compositions  $0 \leq x < 0.1$  remained stable only in a narrow low  $T$ -high  $P_{\text{O}_2}$  region and their modulation period changed stepwisely, not continuously, and reversibly between 4.9b (oxidized) and 5.5b (reduced) when the oxygen content was changed only by 0.65%. In relation to this we propose for  $0 \leq x < 0.1$  specifically that the change in oxygen content induces the exchange of small amounts of Bi and Sr ions between the "BiO" and "SrO" sheets. The superconductivity of the cation-stoichiometric composition ( $x = 0$ ) was also studied as a function of oxygen content.

Keywords: Phase diagram /  $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+\delta}$  / Substitution / Modulation / Superconductivity

The "2201" phase in the  $\text{Bi}_2\text{O}_3$ -SrO-CuO system is known to adapt itself to various Bi:Sr:Cu ratios. Our previous phase diagrammatic study done at 840°C in the air [1] showed that the monophasic range was  $0.1 < x < 0.6$  and  $0 < y < x/2$  for  $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{Cu}_{1+y}\text{O}_z$  and that for  $0 \leq x \leq 0.1$  three kinds of phases including the Bi-poorest end of the above mentioned solid solution,  $\text{Bi}_{17}\text{Sr}_{16}\text{Cu}_7\text{O}_z$ , and  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$  co-existed. More recently it has been reported that the solubility range is extended toward  $x = 0$  at high oxygen pressures. Kato et al. successfully obtained a cation-stoichiometric sample with  $x = 0$  at 840°C and  $P_{\text{O}_2} = 30$  atm, which was an over-doped metal that became a superconductor when annealed in  $\text{N}_2$  [2].

In this report we will shed a new light on the relation among Bi content, oxygen content, thermal stability, and structural features of the 2201 phase by comparing behaviors of monophasic samples with  $0 \leq x \leq 0.4$  systematically which were all prepared under conventional conditions like  $P_{\text{O}_2} = 1$  atm and 800°C.

All the samples were prepared by an ordinary ceramic

method from  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ , and CuO, each with a purity of 99.9%. Appropriate mixtures of these starting materials were pressed into pellets and heated at 600°C-840°C for 20h-120h in total with intermittent grinding, mixing and pelletizing processes. Three different atmospheres including an oxygen stream of 1 atm, the air, and an Ar stream of 1 atm were used. Certain samples were post-annealed in the Ar atmosphere at different temperatures between 200-700°C for 12-240h depending upon the temperature.

Cation-stoichiometric  $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$  was successfully obtained by firing the starting mixture in flowing  $\text{O}_2$  first at 720°C and finally at 800°C. The tetragonal cell parameters of  $a = 5.361$  Å,  $c = 24.65$  Å calculated from the X-ray diffraction peaks were almost identical to those ( $a = 5.37$  Å,  $c = 24.65$  Å) of Kato et al.'s sample with  $\delta = 0.2$  which was synthesized under  $P_{\text{O}_2} = 30$  atm and post-annealed in flowing  $\text{N}_2$ . We note here that small amounts of  $\text{Bi}_{17}\text{Sr}_{16}\text{Cu}_7\text{O}_z$  and others were detected after a further treatment at 820°C, showing the stability of  $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$ .

## SOLID STATE CHEMISTRY — Quantum Spin Fluids—

### Scope of research

Quantum oxide systems such as high- $T_c$  superconducting cuprates,  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and a spin-ladder,  $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}$  are synthesized in the form of single crystals using traveling-solvent-floating-zone and laser abrasion techniques. Detailed equilibrium phase diagram of Bi cuprate systems is investigated. Main subjects and techniques are: mechanism of high- $T_c$  superconductivity: origin of quantum phase separation in strongly correlated electron systems: spin excitations in quantum spin systems: interplay between spin and charge flow in doped spin systems: neutron scattering by using triple-axis as well as time-of-flight techniques.



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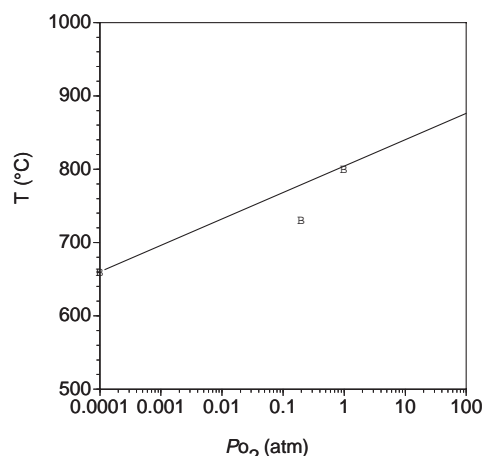
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**Figure 1.** Temperature-oxygen pressure diagram with a border line below which the cation-stoichiometric composition remains stable. The closed squares are the present data and the open square is from ref. 2.

being limited to  $T \leq 800^\circ\text{C}$  at  $P_{\text{O}_2} = 1$  atm.

We tested the synthesis at a lower oxygen pressure as follows. Shown in Fig. 1 is a  $P_{\text{O}_2}$ - $T$  diagram with a border line below which the cation-stoichiometric composition remains stable.

Monophasic samples with higher Bi contents of  $0 < x \leq 0.4$  were also prepared at both  $(T/^\circ\text{C}, P_{\text{O}_2}/\text{atm}) = (800, 1)$  and  $(730, 0.2)$ . The composition dependences of the lattice parameters,  $a$  and  $c$ , are plotted in Fig. 3. As Bi content increases from  $x = 0$  to 0.4, the  $c$  parameter decreased by 0.8%, while  $a$  increased by 0.6%. In further detail, the  $c$  parameter showed a small jump at  $x \approx 0.1$  and, at the same time, the slope,  $da/dx$ , became sharper for  $0.1 \leq x$ . This anomaly concerning the lattice parameters is one of the several features that separate the composition range of  $0 \leq x \leq 0.4$  into two with a border line at  $x \approx 0.1$ .

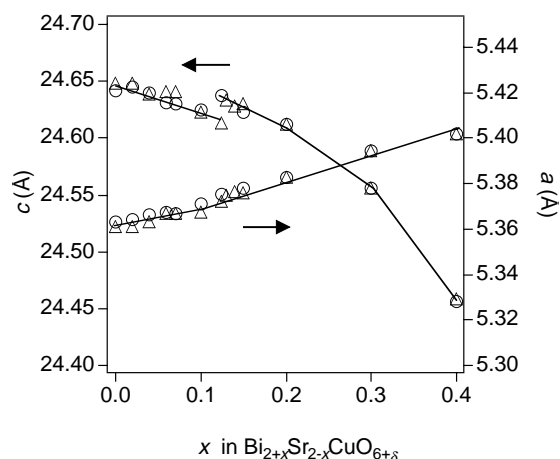
In parallel to this, the thermal stability examined at  $P_{\text{O}_2} = 0.2$  atm and 1 atm also showed a gap at  $x \approx 0.1$ . Saying typically, the decomposition temperature was as high as  $\approx 880^\circ\text{C}$  for  $x = 0.125$  in the air but it dropped to  $\approx 780^\circ\text{C}$  for  $x = 0.10$  in the same atmosphere.

It is well-known that the 2201 structure is incommensurately modulated with its wave vector,  $q$ , lying in the  $b^*-c^*$  plane. We found the same type of modulation in all the present samples by means of XRD and TEM. The coefficients  $b_m$  and  $c_m$  of the vector  $q = b_m b^* + c_m c^*$  showed an interesting stepwise composition dependence again at  $x \approx 0.1$ . These coefficients were evaluated from the XRD data using the following equation

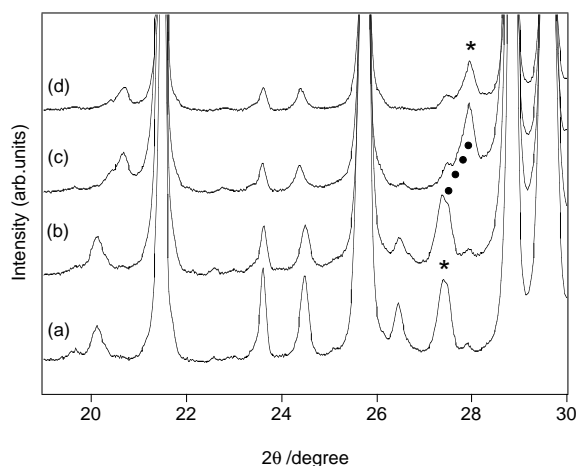
$$1/d_{hklm}^2 = h^2/a^2 + (k+mb_m)^2/b^2 + (l+mc_m)^2/c^2, \quad (1)$$

where  $d_{hklm}$  stands for the  $d$  value of a superlattice peak ( $hkl, \pm m$ ). We obtained a set of parameters ( $a=b/\text{\AA}$ ,  $c/\text{\AA}$ ,  $b_m, c_m$ ) = (5.361, 24.65, 0.205, 0.455) from the XRD pattern for the  $x = 0$  sample prepared at  $800^\circ\text{C}$  and  $P_{\text{O}_2} = 1$  atm.

Through a cyclic treatment of the former sample at  $730^\circ\text{C}$  in the air and at  $800^\circ\text{C}$  in flowing  $\text{O}_2$  we noticed that the change was quite reversible. We further noticed that  $b_m$  and  $c_m$  were changed stepwisely, not continuously, from  $(b_m, c_m) = (0.205, 0.455)$  to  $(0.185, 0.288)$  by reducing treatments as can be seen most typically for the sample annealed at  $400^\circ\text{C}$  in Ar (see Fig.3). These two types are mixed in samples annealed under intermediate conditions



**Figure 2.** Composition dependence of the subcell lattice parameters. The triangles are for the samples prepared at  $800^\circ\text{C}$  in  $\text{O}_2$ , and the circles are for those prepared at  $730^\circ\text{C}$  in the air.



**Figure 3.** Partial enlargements of the XRD patterns of  $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$  as-prepared in  $\text{O}_2$  at  $800^\circ\text{C}$  (a), post-annealed in Ar at  $200^\circ\text{C}$  (b),  $400^\circ\text{C}$  (c), and  $600^\circ\text{C}$  (d).

like  $730^\circ\text{C}$  in the air. There seems no doubt that a slight change in oxygen content switches the modulation mode from one to the other, without changing the  $a$  and  $c$  parameters remarkably.

We conducted TEM observations on the two typical samples with  $x = 0$ , one as-prepared in  $\text{O}_2$  and the other annealed in Ar at  $600^\circ\text{C}$ . The modulation wavelength varied from  $\lambda = 4.9b$  for the as-prepared sample to  $\lambda = 5.5b$  for the annealed one, which are consistent with the XRD results of  $\lambda = 4.88b (= b/0.205)$  and  $5.41b (= b/0.185)$ , respectively.

From the resistance and magnetization measurements it has been revealed that it is only the portion with  $(b_m, c_m) = (0.185, 0.288)$  that is superconducting but the portion with  $(b_m, c_m) = (0.205, 0.455)$  is an over-doped metal.

## References

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